Reactive Minerals in Aquifers: Formation Processes and Quantitative Analysis

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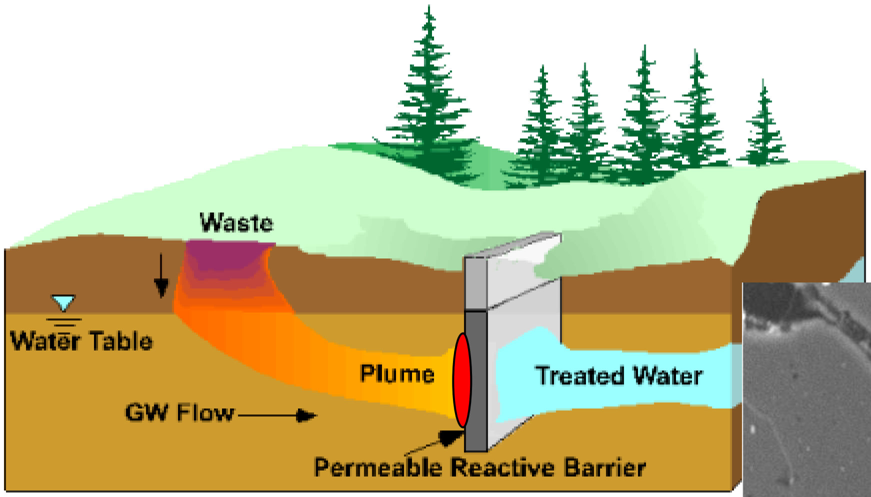
Degradation Processes

- **Understanding Attenuation Mechanisms**
  - **Decoupling biotic/abiotic contributions**
- **Biotic Processes**
  - **Reductive dechlorination**
  - **Microbial communities**
- **Abiotic Processes**
  - **Hydrolysis, Reductive elimination**
  - **Mineral-water interface**
  - **MNA for inorganic contaminants**

Presentation Goals/Outline

- Identify candidate phases: Fe-S-C-O
- Mineral stability/transformation
- Tools for site characterization:
  - Geochemical modeling
  - Solid-phase characterization

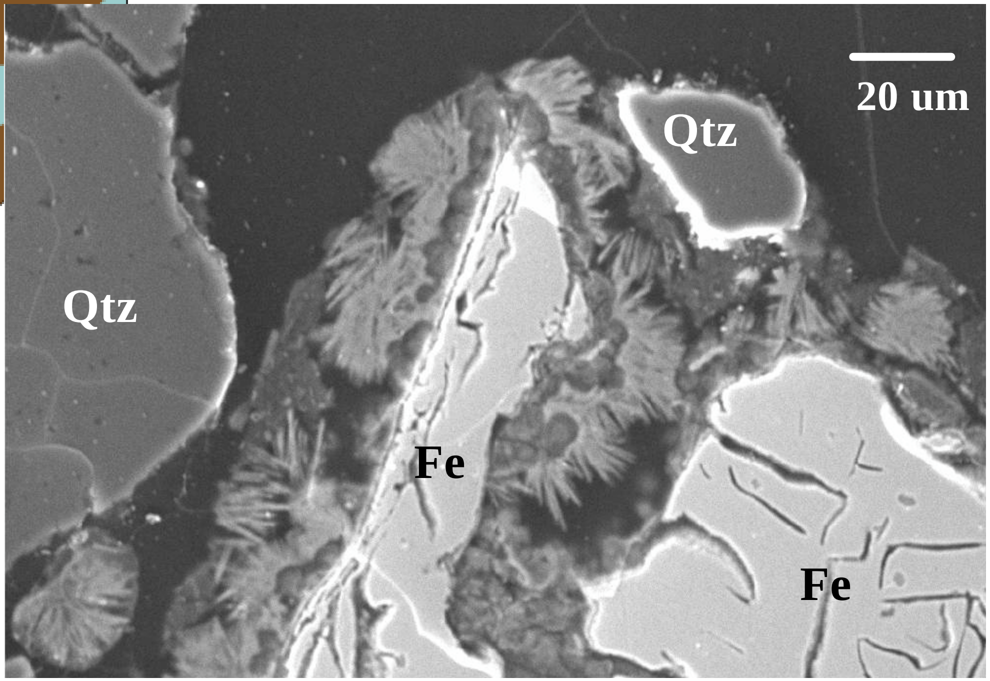
Permeable Reactive Barriers



Upgradient Interface Region

Surface Precipitates: Fe-S-C-OH

- Remove pore volume
- Mask reactive Fe^0 sites
- Provide new reactive sites?



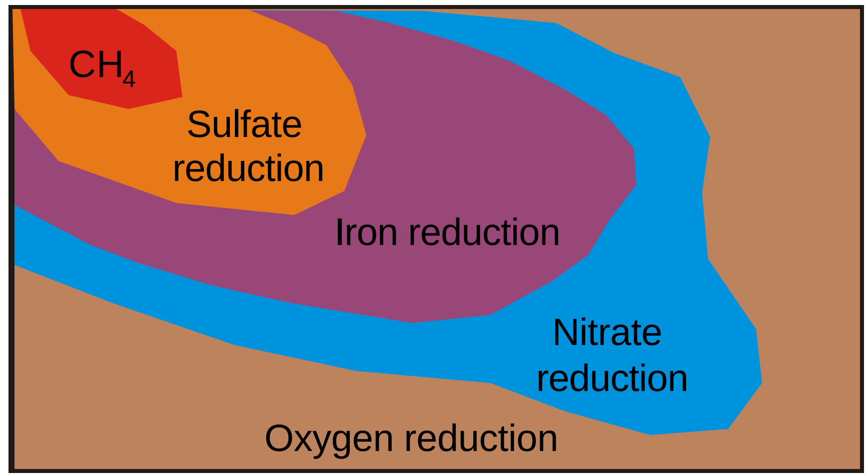
Redox Processes: Aquifers

Fe RBs

$$e^- + Fe(III) \Rightarrow Fe^{2+}$$

Organic Carbon

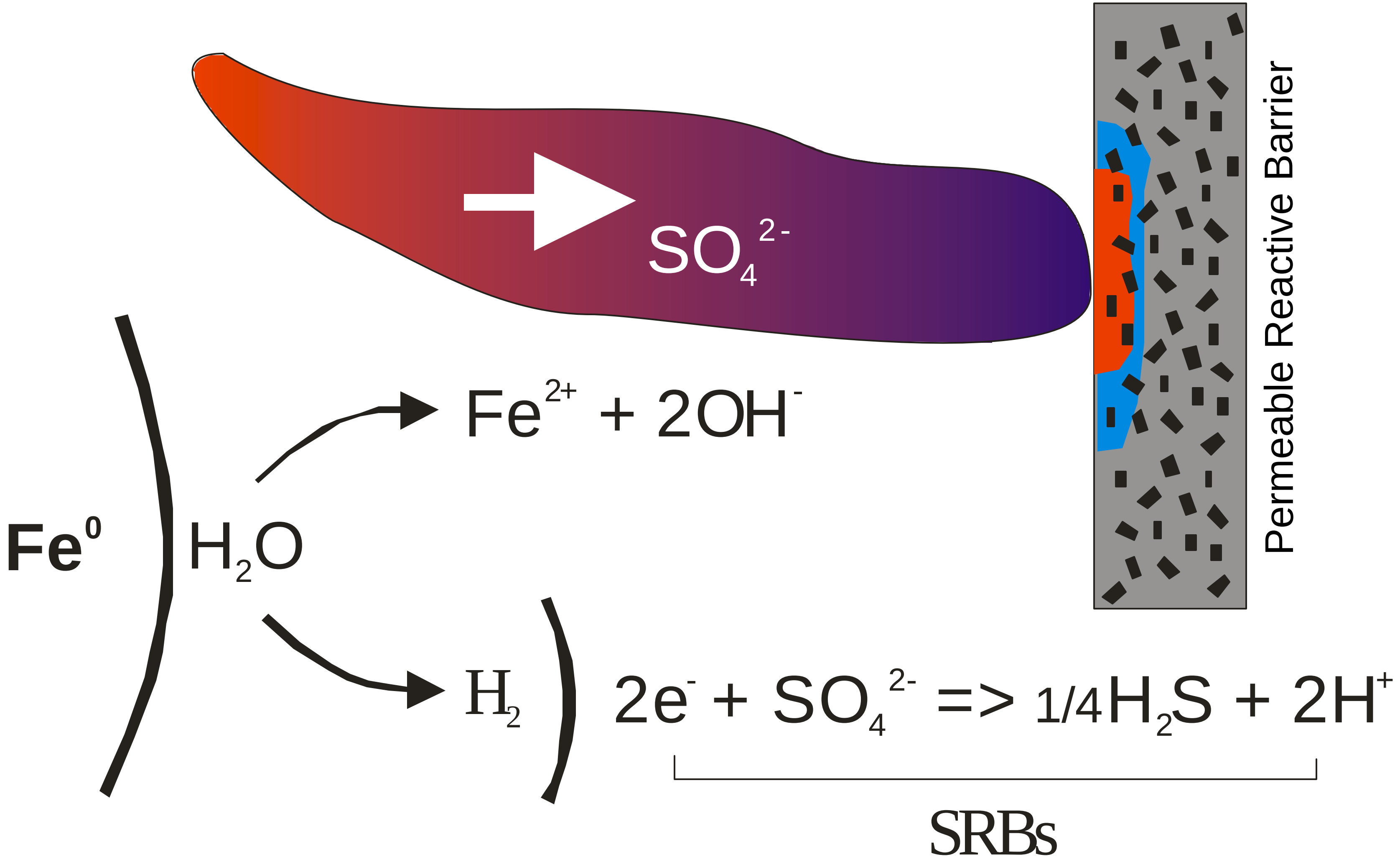
HCO_3^-



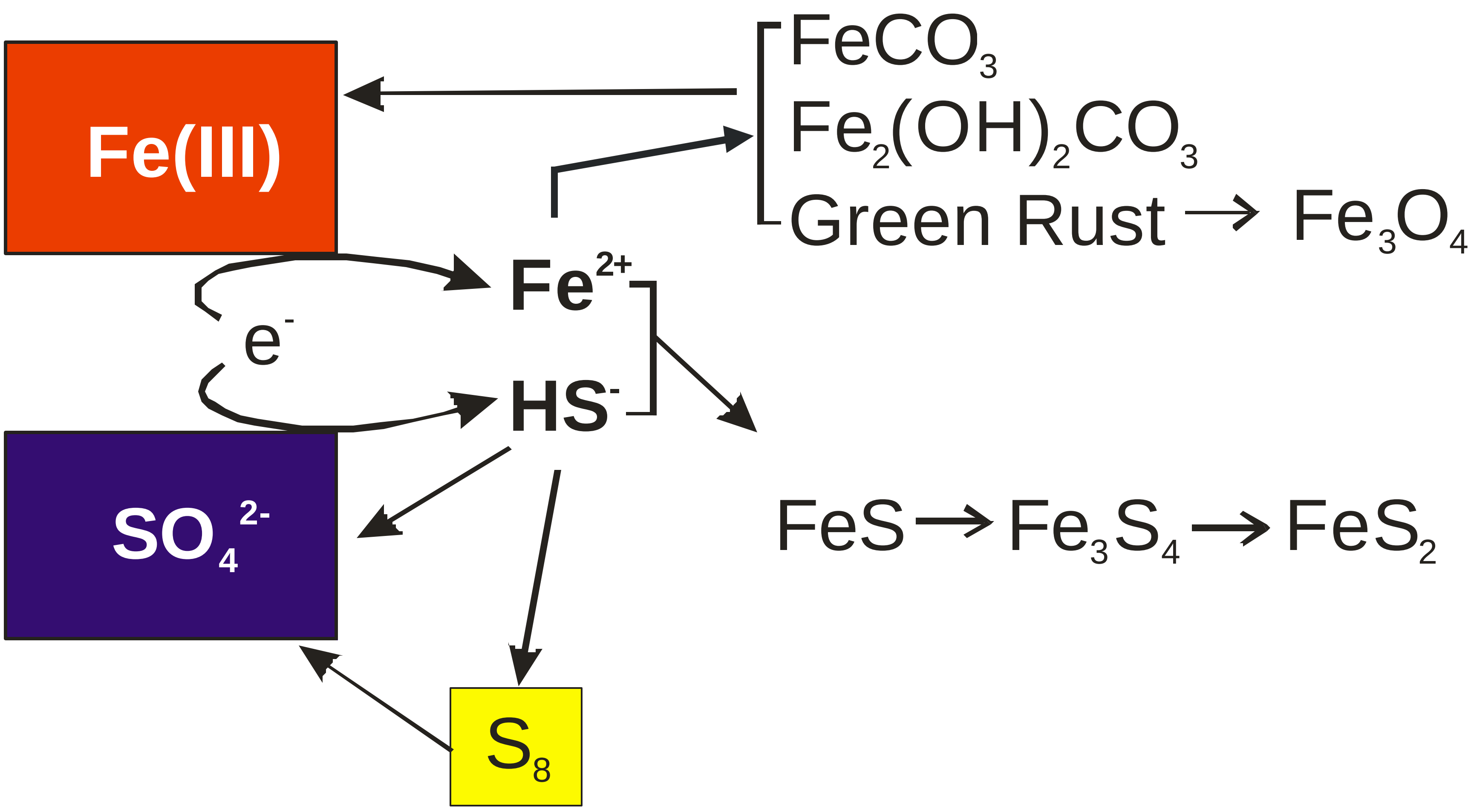
$$8e^- + SO_4^{2-} \Rightarrow H_2S/HS^-$$

SRBs

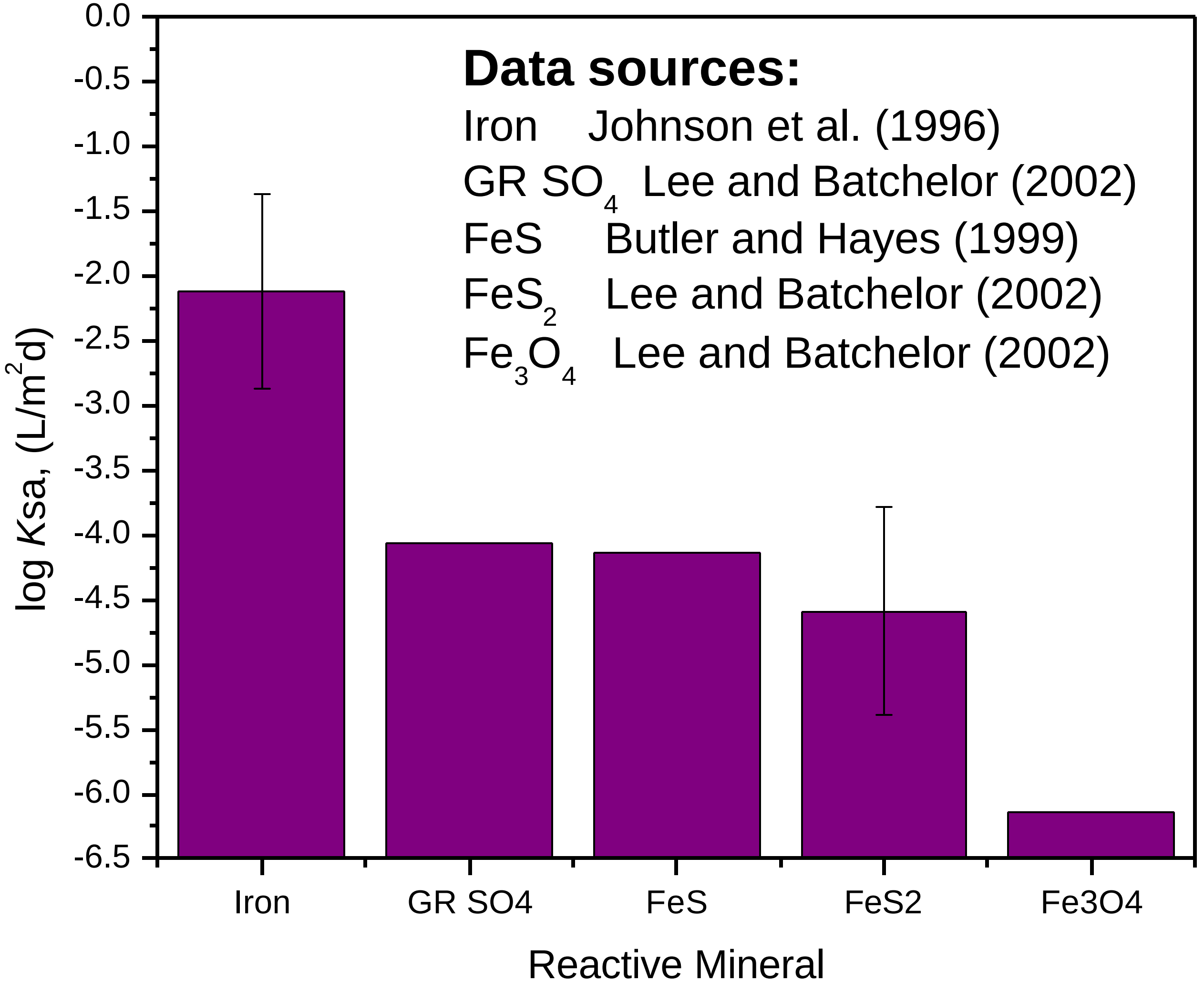
Redox Processes: PRBs



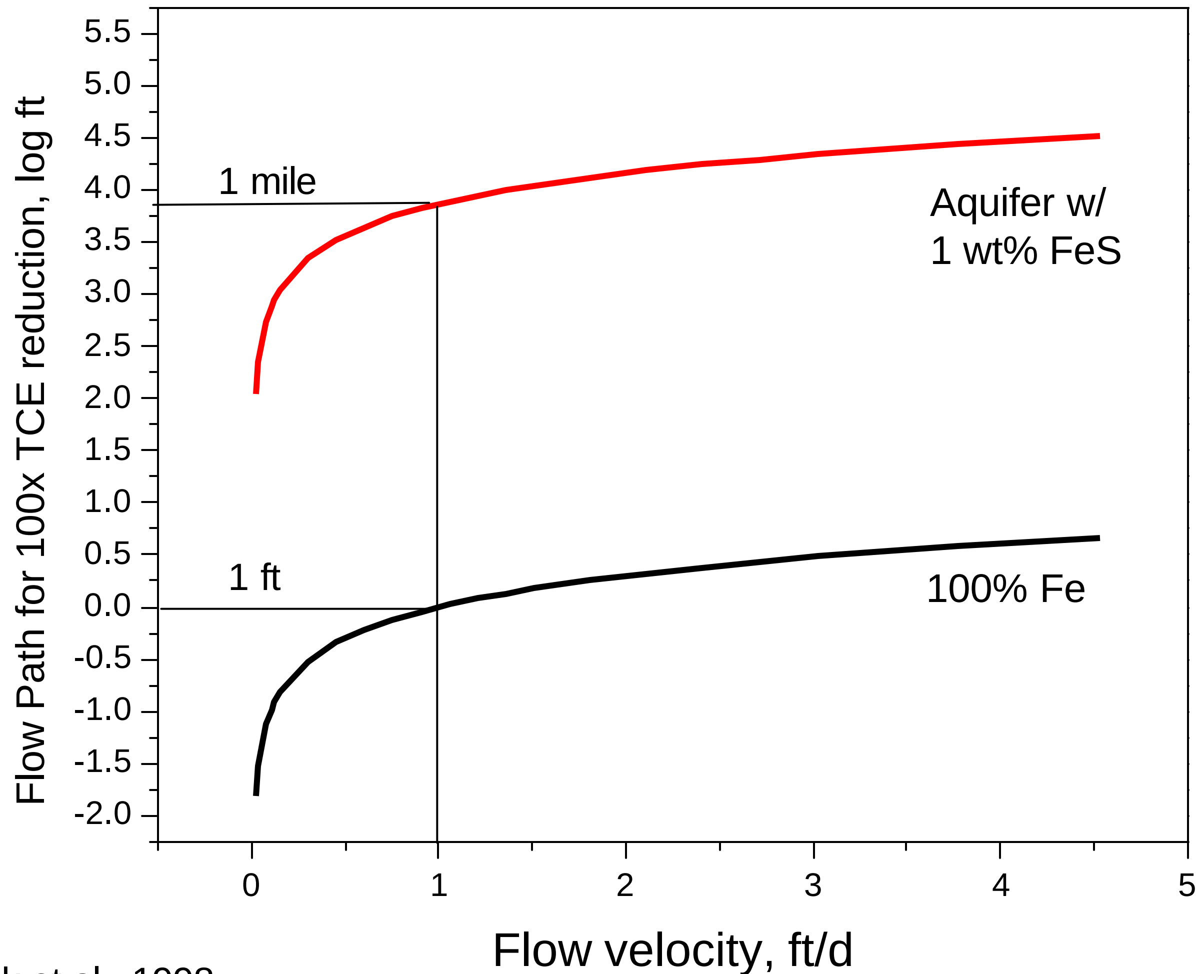
Reactive Minerals/Formation



TCE Reaction Rates



Rate Comparison

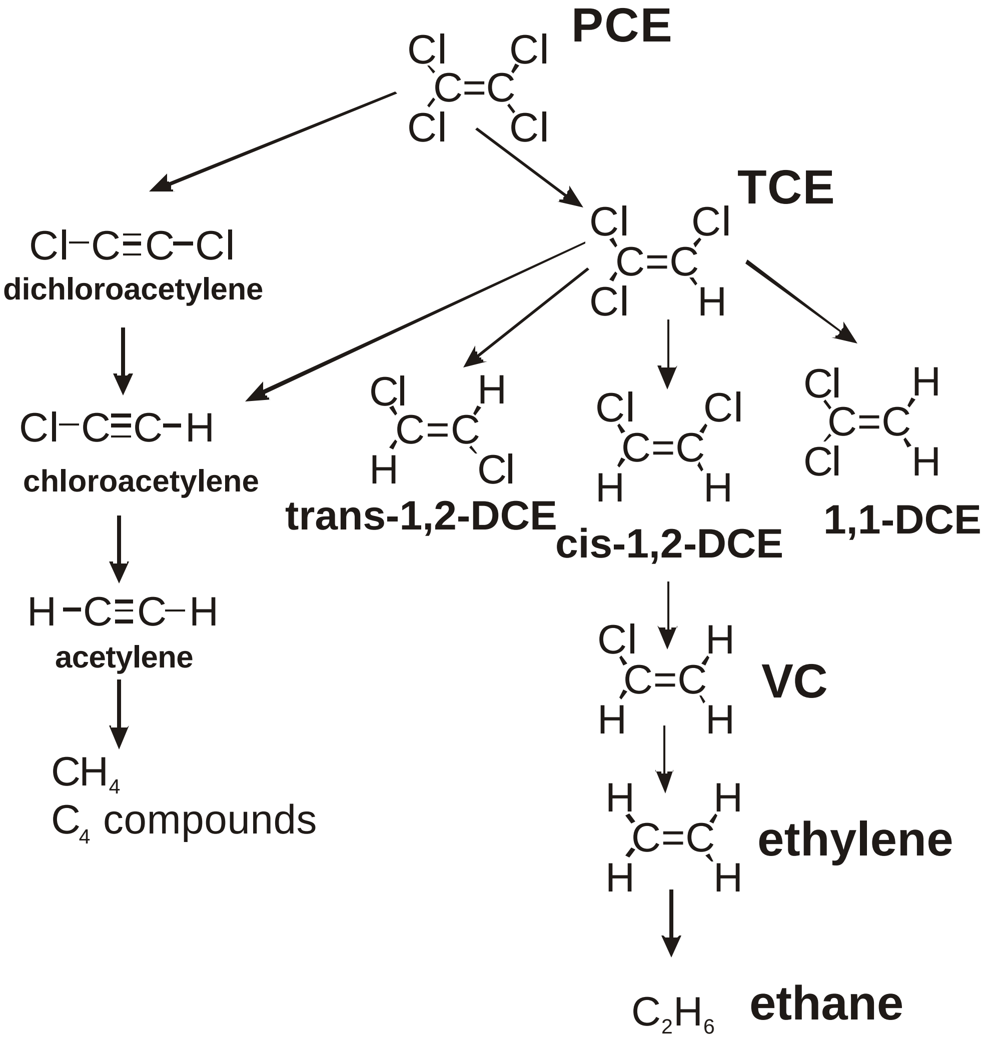


1D-model: Tratnyek et al., 1998

Contaminant Transformation

Abiotic Degradation Pathways

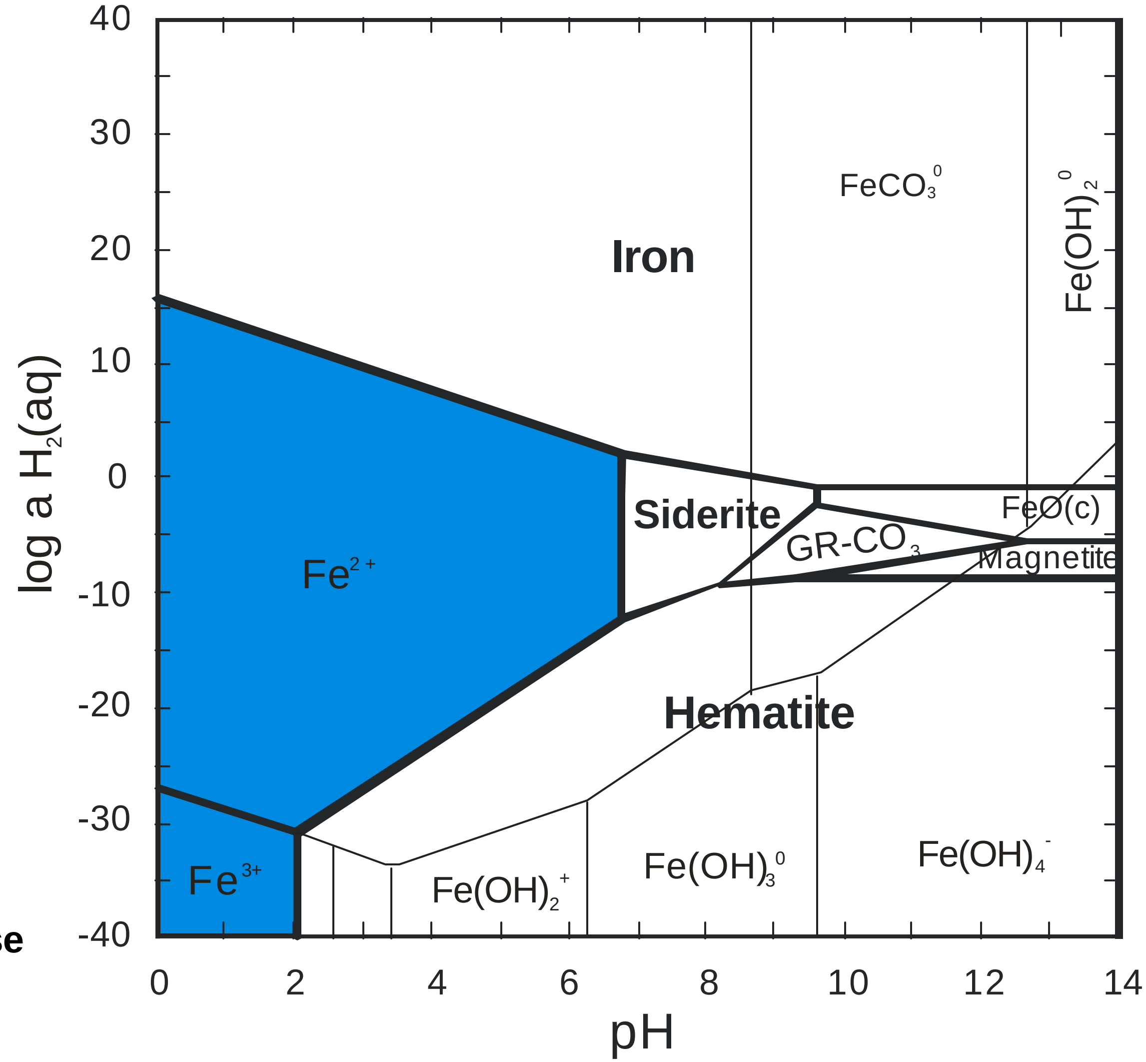
Biotic Degradation Pathways



Identifying Reactive Minerals

- Geochemical conditions: pH and redox
- Solution composition: comparing ion activity products to *K*sp
  - Thermodynamic data for solids and aqueous species
  - Input data for activity coefficients
- Solid-phase characterization
  - Sample collection and handling
  - Bulk elemental composition
  - Extraction procedures for element partitioning
  - Mineralogical characterization

Mineral Stability: Redox-pH



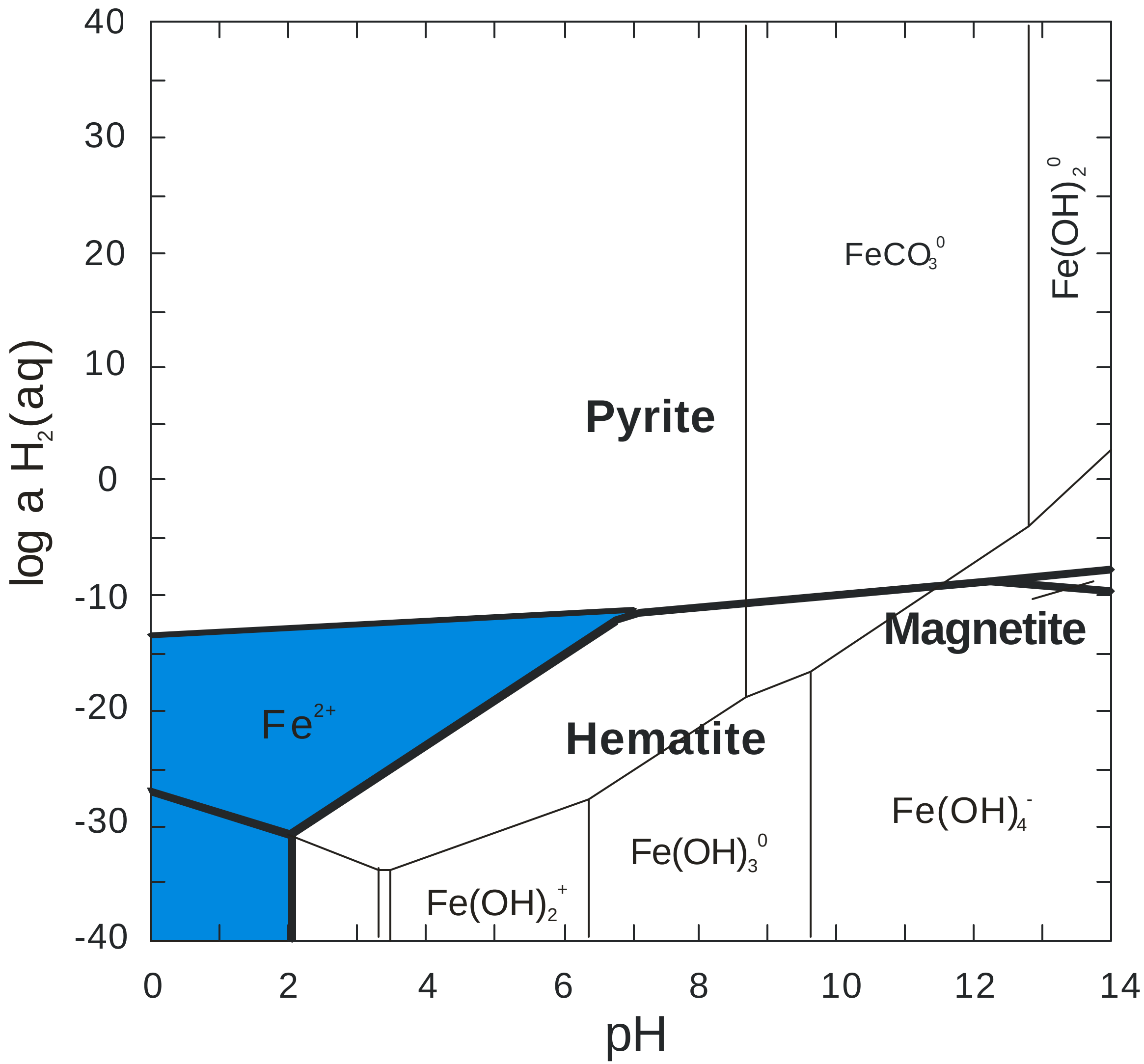
25°C

$\Sigma C = 10^{-2}$

$\Sigma Fe = 10^{-5}$

EQ3/6 database w/additions (Fe^0, GR, FeS)

Mineral Stability: Redox-pH



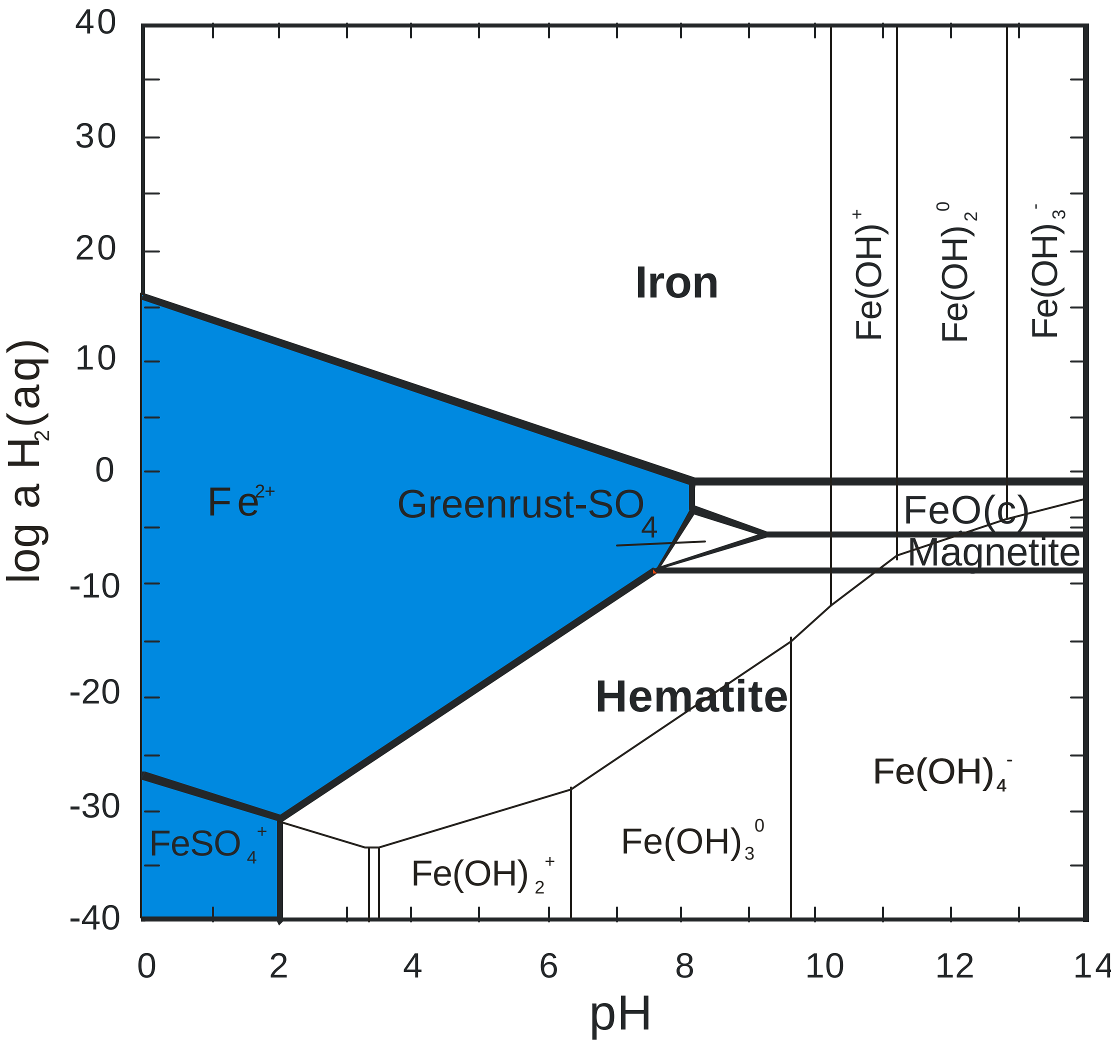
25°C

$\Sigma S = 10^{-3}$

$\Sigma C = 10^{-2}$

$\Sigma Fe = 10^{-5}$

Mineral Stability: Redox-pH



25°C

$\Sigma S=10^{-3}$

$\Sigma Fe=10^{-5}$

- Suppress all Sulfide Minerals

Eh-pH Method

- **Information about equilibrium aqueous species and solids displayed**
- **Redox and pH – relevant master variables**
- **Limitations in defining redox condition:**
  fO_2, fH_2, Eh, Fe(II)/Fe(III)
- **Built-in assumptions, choice & content of database; phase suppression**
- **Interpretation: will a particular phase be present or not?**

Identifying Reactive Minerals

- Geochemical conditions: pH and redox
- Solution composition: comparing ion activity products to *K*sp
  - Thermodynamic data
  - Input data for activity corrections
- Solid phase characterization
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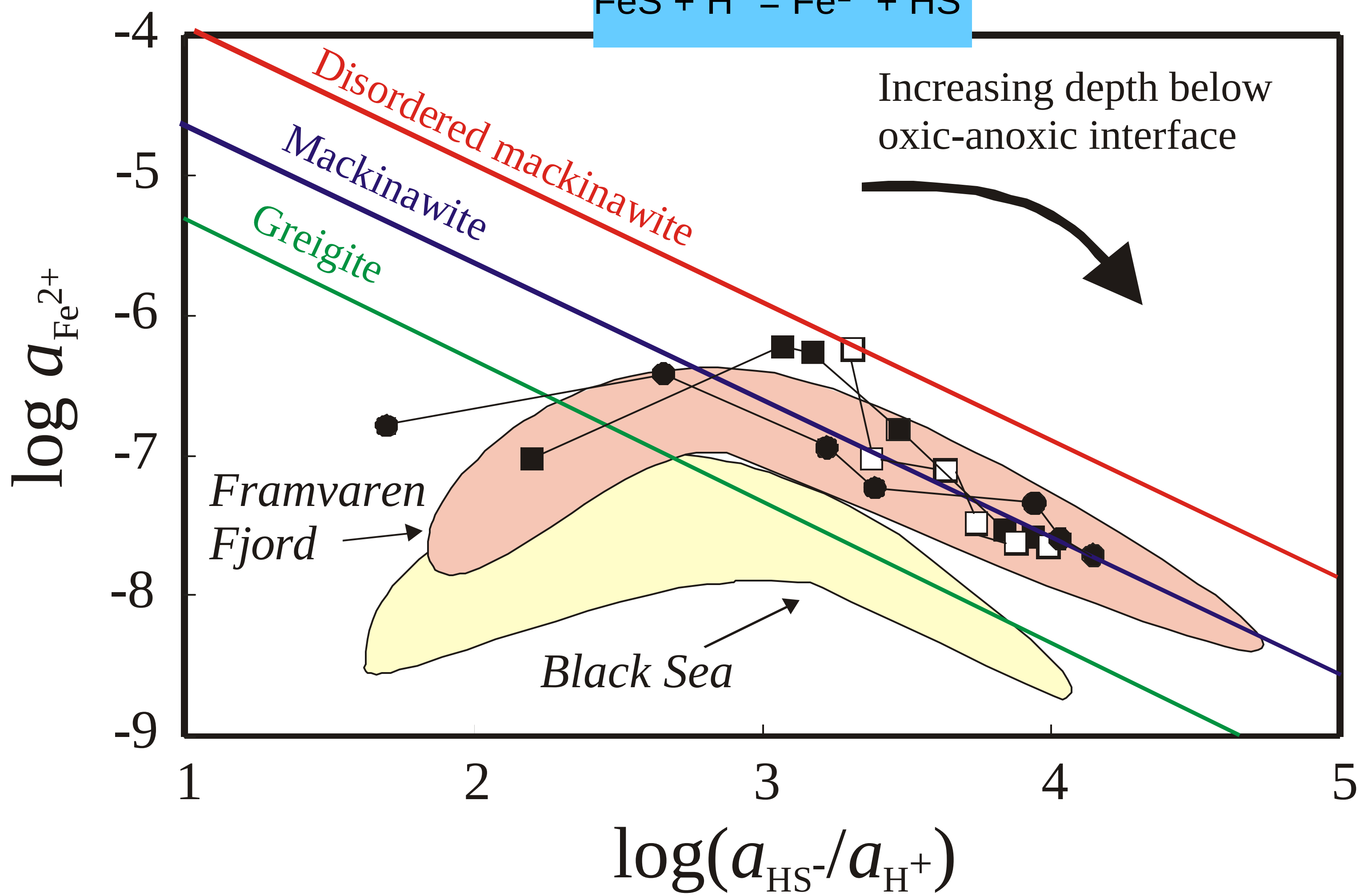
IAP Approach

$FeS + H^+ = Fe^{2+} + HS^-$



Fe(II)/Fe(III) problem

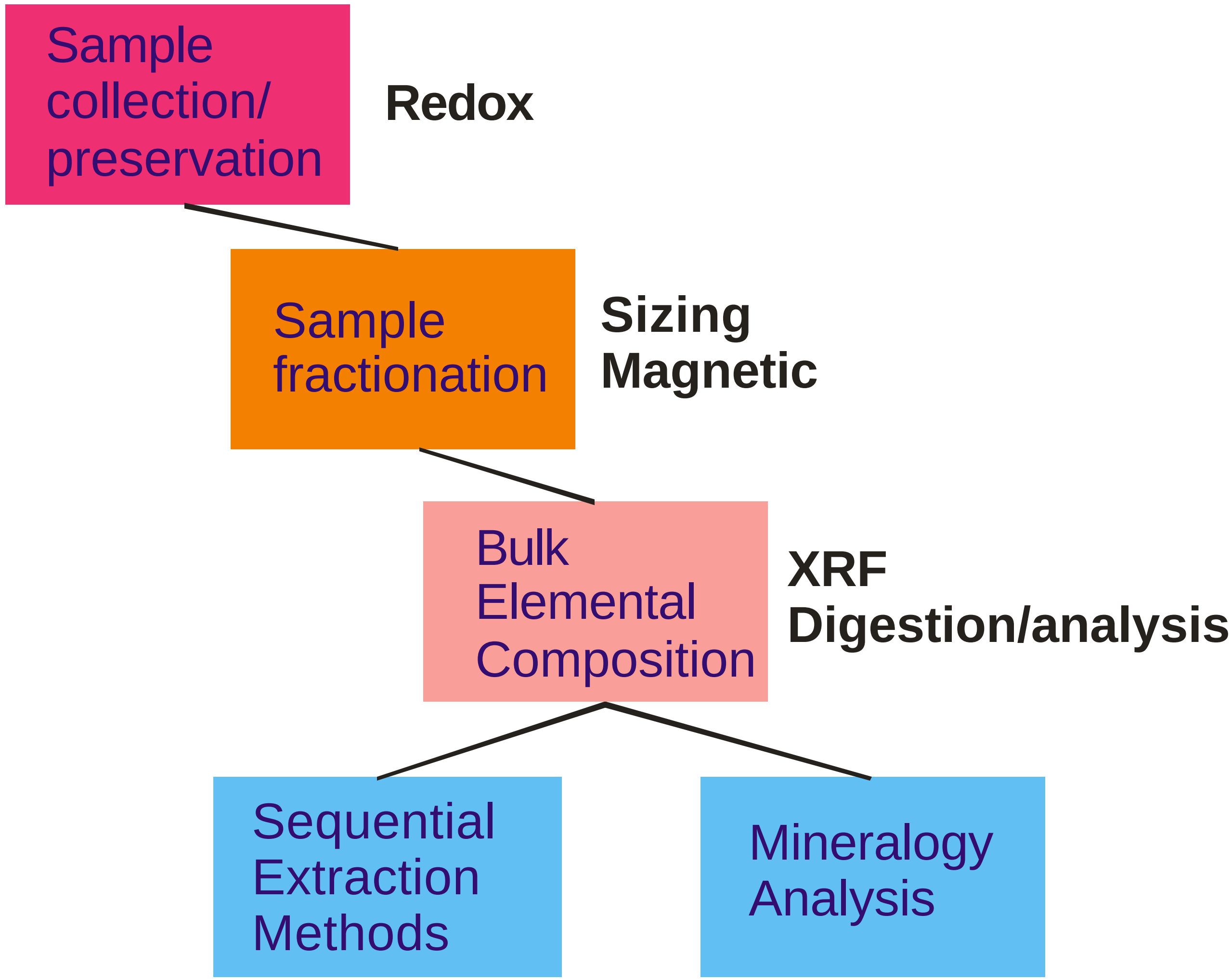
$Fe_6(OH)_{12}CO_3 + 13H^+ = 4Fe^{2+} + 2Fe^{3+} + HCO_3^- + 12H_2O$

log K = 29.73
IAP calculation requires both Fe(II) and Fe(III)

Approaches:

- **Measure both Fe(II) and Fe(III)**
- **Use Eh as master redox variable**
- **Measure Fe(II), calculate Fe(III) by assuming control by Fe-OH solubility**
- **Use some other measured redox pair to fix Fe(II)/Fe(III)**

Solid-Phase Characterization

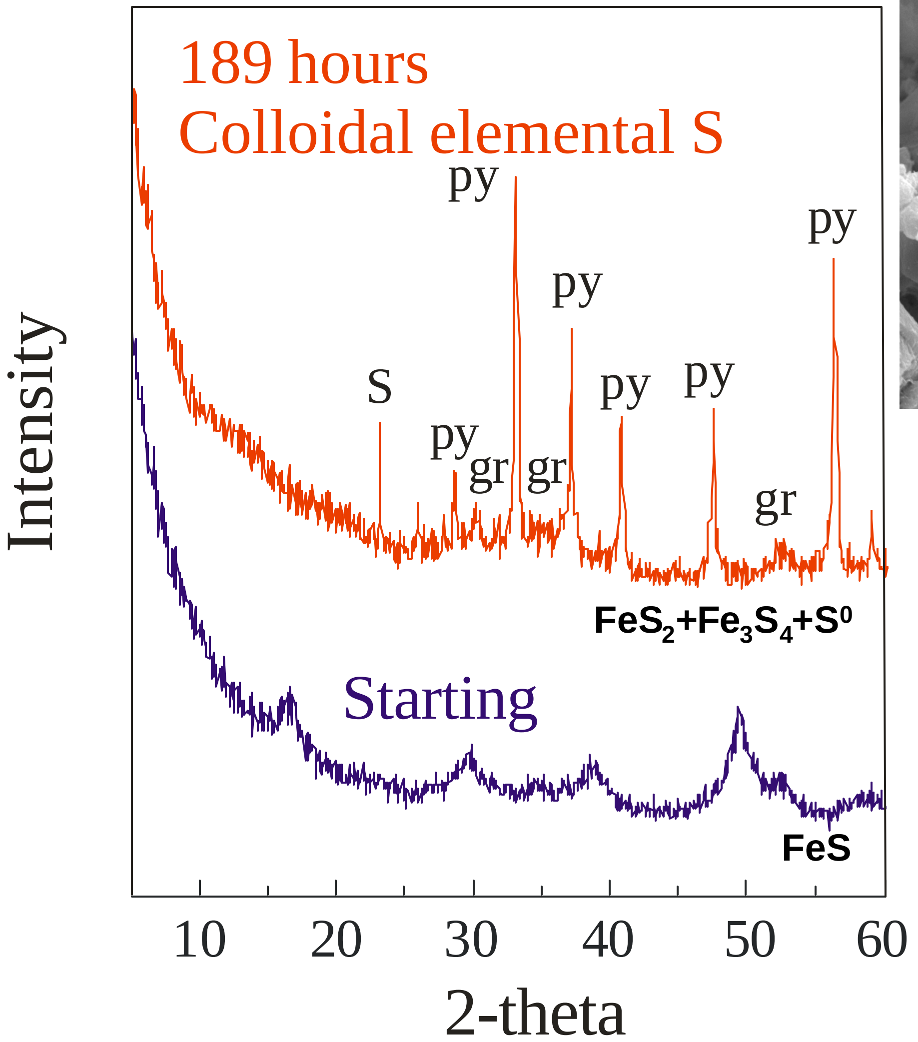


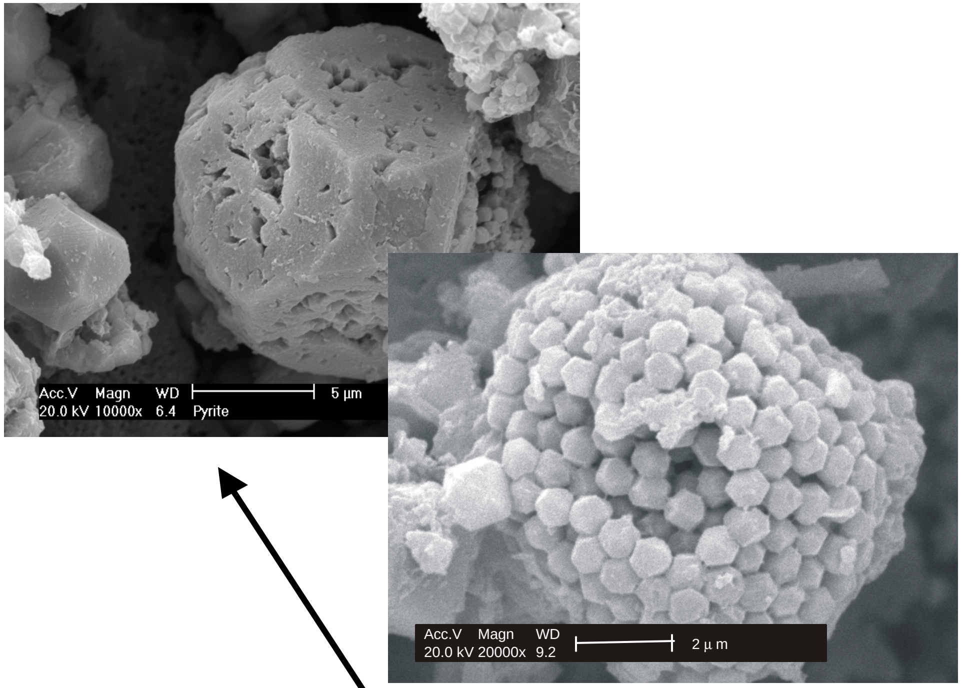
Analytical Methods

- **Sample-Destructive Elemental Analysis**
  - Digestion followed by AAS, AFS, ICP-ES/MS
  - Elemental analyzers (e.g., C, S, N)
- **Sample-Non-Destructive Elemental Analysis**
  - XRF, SEM-EDS/WDS
- **Mineralogy**
  - X-ray Diffraction
  - Infrared Spectroscopy
  - Raman Spectroscopy
  - X-ray Absorption Spectroscopy
- **Other**
  - Optical microscopy
  - Thermal analysis
  - Selective extractions

See Amonette (2002)

Iron Sulfide Transformations





“slow transformation”

“fast transformation”

FeS Starting material

FeS-to-FeS_2 Kinetics

- Redox:

  Highly reducing conditions: transformation rate is slow (years, pH 7)

  Moderately reducing conditions: transformation rate is fast (days to months, pH 7)

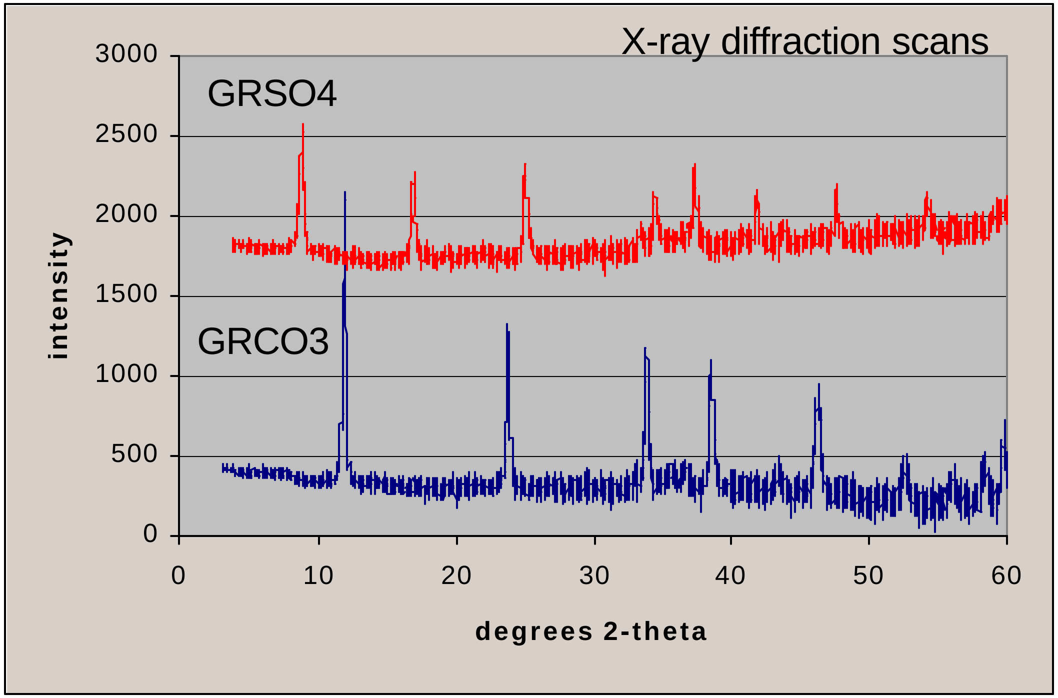
- pH:

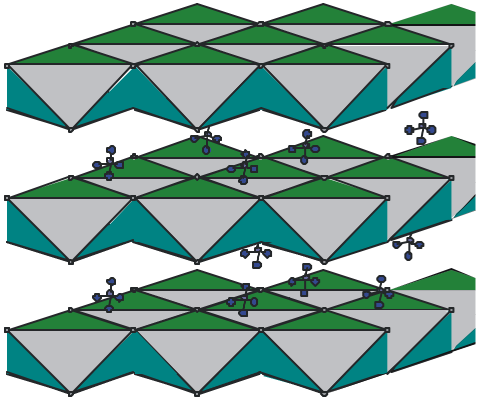
  Transformation rate decreases w/increasing pH

- Preparation of Precursor:

  Filtration, freeze-drying, $\Sigma Fe/\Sigma H_2S$ in solution

Green Rust





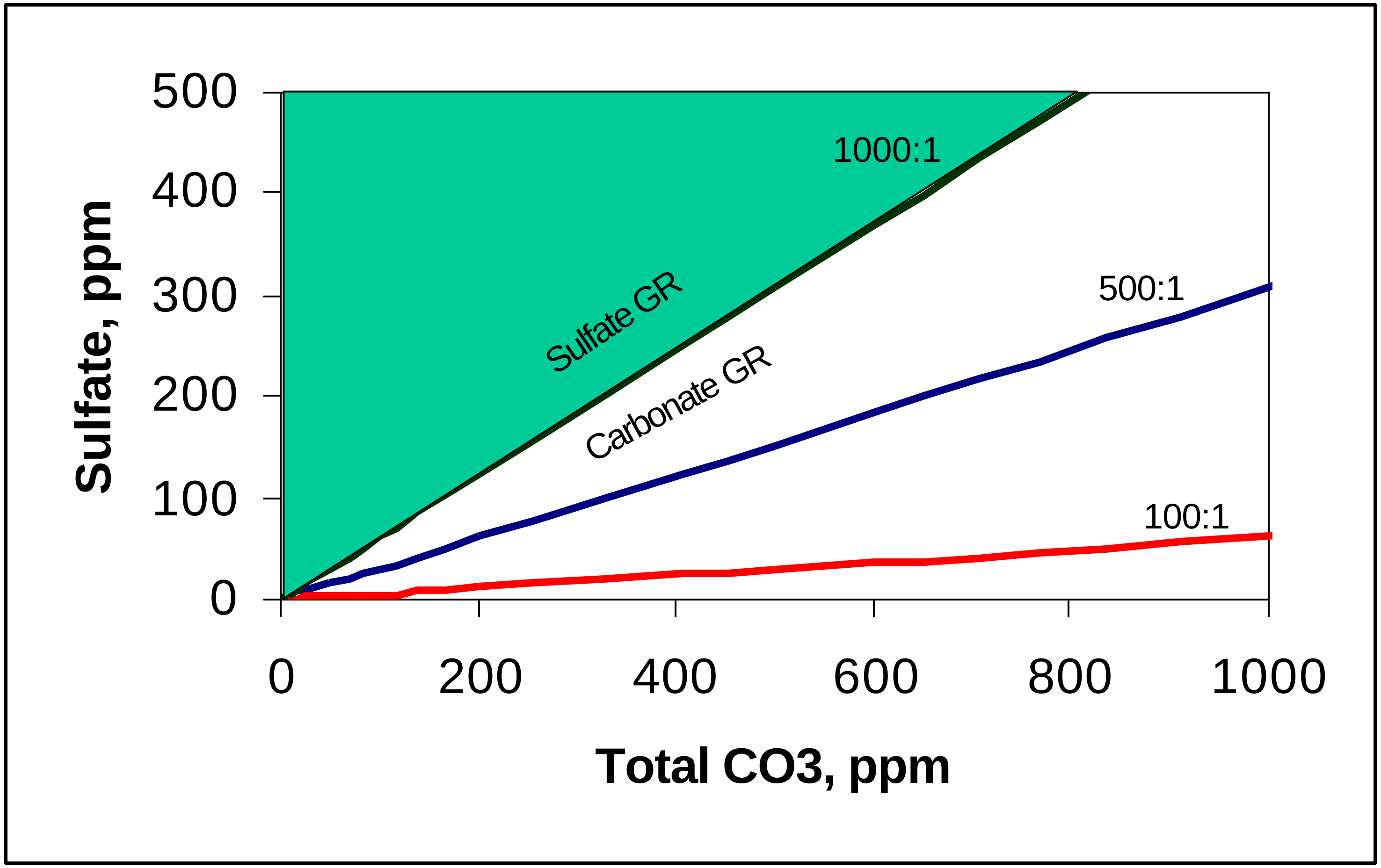
GRCO3 = 0.8 nm
GRSO4 = 1.1 nm

$$\mathbf{Fe_6(OH)_{12}SO_4 + CO_3^{2-} = Fe_6(OH)_{12}CO_3 + SO_4^{2-}}$$

$$K_1 = [SO_4^{2-} / CO_3^{2-}] \cdot [Fe_6(OH)_{12}CO_3 / Fe_6(OH)_{12}SO_4] = 10^{3.1}$$

GR free energy data from Bourrié et al. (1999)

Sulfate vs. Carbonate GR



pH 7

Conclusions

- Experimental evidence for abiotic reduction pathways
- Continued need for experimental results/dynamic-flow systems
- Deconvoluting biotic/abiotic contributions
  - Reactive mineral identification/quantification
  - Stable isotope tools
  - Transformation products
- Reactive minerals are vulnerable to transformation